

[TDCC Form Similar to: Form PTO-1390]		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 43040
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) 10/089741
INTERNATIONAL APPLICATION NO. PCT/US00/28563	INTERNATIONAL FILING DATE 13 October 2000	PRIORITY DATE CLAIMED 20 October 1999	
TITLE OF INVENTION CATALYTIC POWDER AND ELECTRODE MADE THEREWITH			
APPLICANT(S) FOR DO/EO/US Yu-Min Tsou; Edmond L. Manor			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.			
2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.			
3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).			
4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.			
5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))			
a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).			
b. <input type="checkbox"/> has been transmitted by the International Bureau.			
c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States receiving Office (RO/US).			
6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).			
7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))			
a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).			
b. <input type="checkbox"/> have been transmitted by the International Bureau.			
c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.			
d. <input checked="" type="checkbox"/> have not been made and will not be made.			
8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).			
9. <input type="checkbox"/> An oath or declaration of the inventor (35 U.S.C. 371(c)(4)).			
10. <input type="checkbox"/> A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).			
Items 11. to 15. below concern other document(s) or information included:			
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.			
12. <input type="checkbox"/> A FIRST preliminary amendment.			
<input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.			
13. <input type="checkbox"/> A substitute specification.			
14. <input type="checkbox"/> A change of power of attorney and/or address letter.			
15. <input type="checkbox"/> Other items or information:			

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <div style="font-size: 1.5em; font-weight: bold;">10,089741</div>	INTERNATIONAL APPLICATION NO. PCT/US00/28563	ATTORNEY'S DOCKET NUMBER 43040
--	--	--

17. <input checked="" type="checkbox"/> The following fees are submitted: <div style="margin-left: 20px;"> Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$ 890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$ 710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$ 740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO \$ 1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 </div> <div style="text-align: right; margin-top: 10px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>	CALCULATIONS	PTO USE ONLY
Surcharge of \$ 130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	+ \$ 130.00	

Claims	Number Filed	Number Extra	Rate		
Total Claim	27 - 20 =	7	X \$ 18.00	\$ 126.00	
Independent Claims	3 - 3 =	0	X \$ 84.00	\$ 0.00	
Multiple dependent claim(s) (if applicable)			\$ 0.00	\$ 0.00	

Processing fee of \$ 0 for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	+ \$ 0.00	
TOTAL NATIONAL FEE =		
\$ 1,146.00		

	Amount to be refunded:	\$
	charged:	\$

a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. **04-1512** in the amount of \$ **1,146.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **04-1512**. A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Graham E. Taylor The Dow Chemical Company Intellectual Property P.O. Box 1967 Midland, Michigan 48641-1967 UNITED STATES OF AMERICA Phone: (989) 636-2880	Signature: <u><i>Elisabeth T. Jozwiak</i></u> Elisabeth T. Jozwiak , Registration No. 41.101 Date: <u>02 April 2002</u>
---	--

PTO/PCT Rec'd 02 APR 2002

CATALYTIC POWDER AND ELECTRODE MADE THEREWITH

The present invention is directed to electrocatalytic electrodes. More particularly, the present invention is directed to cathodes useful in electrolysis cells such as a chlor-alkali cell.

Chlorine and caustic soda are typically produced by electrolysis of aqueous solutions of sodium chloride, a process commonly referred to as a chlor-alkali process.

The most widely used chlor-alkali processes employ either diaphragm or membrane type cells. In a diaphragm cell, an alkali metal halide brine solution is fed into an anolyte compartment where halide ions are oxidized to produce halogen gas. Alkali metal ions migrate into a catholyte compartment through a hydraulically-permeable microporous diaphragm disposed between the anolyte compartment and the catholyte compartment. Hydrogen gas and aqueous alkali metal hydroxide solutions are produced at the cathode. Due to the hydraulically-permeable diaphragm, brine may flow into the catholyte compartment and mix with the alkali metal hydroxide solution.

A membrane cell functions similarly to a diaphragm cell, except that the diaphragm is replaced by an hydraulically-impermeable, cation-selective membrane which selectively permits passage of hydrated alkali metal ions to the catholyte compartment. A membrane cell produces aqueous alkali metal hydroxide solution essentially uncontaminated with brine.

Electrodes are usually prepared by providing an electrocatalytic coating on a conducting substrate. Useful catalytic coatings include, for example, the platinum group metals, such as ruthenium, rhodium, osmium, iridium, palladium and platinum. Useful conducting substrates include, for example, nickel, iron, and steel.

Production of chlorine gas at the anode and the concurrent production of the hydroxide ion and evolution of hydrogen gas at the cathode almost always require a cell voltage higher than the thermodynamic energy for the following reaction.



The extra energy, that is, overvoltage, is provided to overcome, among various other parameters, the electrolyte resistance and the overpotential related to the chlorine gas evolution at the anode and the overpotential related to hydrogen gas evolution and hydroxide ion formation at the cathode.

5 Various methods have been proposed to decrease the overpotential requirements of the electrodes by altering surface characteristics. The term "overvoltage" is used herein to refer to the excess voltage required for an electrolytic cell, while the term "overpotential" is used herein to refer to the excess voltage required for an individual electrode within the electrolytic cell.

10 The overpotential for an electrode is a function of its chemical characteristics and current density. Current density is defined as the current applied per unit of actual surface area on an electrode. Techniques which increase the actual surface area of an electrode, such as acid etching or sandblasting the surface of the electrode, result in a corresponding decrease of the current density for a given amount of applied current and also decrease overpotential
15 requirements.

Efforts to reduce overpotential requirements include, for example, those described in U.S. Patent No. 4,66,8370 and U.S. Patent No. 4,798,662, which disclose electrodes useful as cathodes in an electrolytic cell. These are prepared by coating an electrically conducting substrate such as nickel with a catalytic coating comprising one or more platinum group
20 metals from a solution comprising a platinum group metal salt. Both of these Patents disclose electrodes designed to reduce the operating voltage of an electrolytic cell by reducing the overpotential requirements of the electrodes. In addition, U.S. Patent. No. 5,035,789, U.S. Patent. No. 5,227,030, and U.S. Patent. No. 5,066,380 disclose cathode coatings which exhibit low hydrogen overpotentials.

25 A desirable characteristic of a cathode coating is high porosity with large internal surface areas. Large internal surface areas result in lower effective current density and, accordingly, lower overpotentials. Another result of a porous electrode is higher resistance to impurity poisoning. Rough outer surfaces of a typical porous electrode render difficult the electrodeposition of metal ions as impurities and the large internal electroactive surface areas
30 are not easily accessible to the impurity ions present in the electrolyte because of long Pathways for diffusion. Such characteristic is described in U.S. Patent No. 5,645,930

Metal plating is often used to form a reinforcement layer on the electrode. For example, U.S. Patent. No. 4,061,802 and U.S. Patent. No. 4,764,401 describe using palladium chloride to activate plastic or metal substrates prior to nickel plating by electroless deposition.

Figure 1 is a magnified representation of a cross section of a catalytic powder particle
5 of the present invention.

Figure 2 is a magnified representation of a cross section of a portion of an electrode of the present invention.

In one aspect, the present invention is a catalytic powder comprising a plurality of support metal particles comprising a transition metal or an alloy thereof; and a coating
10 surrounding the support metal particles, the coating either comprising an electrocatalytic metal coating or comprising a coating with a metal continuous phase in admixture with a particulate material.

In a second aspect, the present invention is an electrode comprising a conductive metal substrate; and a first layer comprising a matrix with a catalytic powder dispersed
15 therethrough, the matrix comprising a platinum group metal oxide or a mixture of a platinum group metal oxide and a valve metal oxide, the catalytic powder comprising support metal particles covered either with an electrocatalytic metal coating, or with a coating comprising an electrocatalytic metal in admixture with a particulate material.

In a third aspect, the present invention is a process for making an electrode comprising
20 the steps of forming a catalytic powder; mixing the catalytic powder with a dispensing medium to form a mixture; applying the mixture to a conductive metal substrate to form a covered substrate; and baking the covered substrate in the presence of oxygen; and optionally reinforcing the coating adhesion and strength with an alloy coating process.

The present invention is advantageous because a porous coating mixture is first
25 applied to a powder rather than being applied directly to a metal substrate, thereby creating a larger internal surface area relative to the prior art. Large internal surface areas result in lower effective current density and, accordingly, lower overpotentials. Therefore, because the surface area is enhanced using the present invention, the overpotential required for electrodes

made according to the present invention is also reduced relative to electrodes of the prior art cited above.

Figure 1 illustrates a magnified view of a catalytic powder particle 10 of the present invention. As shown, the catalytic powder particle 10 comprises a support metal particle 11 surrounded by a porous coating comprising a continuous phase 12 with a particulate material 13 dispersed therethrough.

Preferably, the support metal particle 11 is a transition metal or alloy thereof. Preferred transition metals include nickel, cobalt, iron, steel, stainless steel or copper. Preferred transition metal alloys include nickel, cobalt, or copper, alloyed with phosphorous, boron or sulfur.

Preferably, the support metal particles, before the porous coating is applied thereto, have an average diameter of at least 0.2 microns, more preferably at least about 1 micron, even more preferably at least 2 microns, and yet even more preferably at least 3 microns. Preferably, the metal particles have an average diameter of up to 20.0 microns, more preferably up to 10.0 microns and even more preferably up to 6.0 microns.

The support metal particle 11 is coated with either an electrocatalytic metal or with a porous coating comprising an electrocatalytic metal continuous phase 12 in admixture with a particulate material 13. Because the coating on the support metal particle is porous and has a dendritic nature, the resulting catalytic powder particle 10 has a large internal surface area with pores 14 throughout.

Preferably, the electrocatalytic metal continuous phase 12 is ruthenium, iridium, osmium, platinum, palladium, rhodium, rhenium, or an alloy of any one or more of these.

In one embodiment, the continuous phase 12 has a particulate material 13 dispersed therethrough. Preferably, particulate material 13 comprises the metal oxides of ruthenium, iridium, osmium, platinum, palladium, rhodium, rhenium, technetium, molybdenum, chromium, niobium, tungsten, tantalum, manganese or lead, with the oxides of ruthenium, iridium osmium, platinum, palladium and rhodium being more preferred..

To make the catalytic powder, a plurality of support metal particles is covered with a porous coating comprising an electrocatalytic metal either alone or in admixture with a

particulate material which comprises either a metal or metal oxide. Generally, the first step in making the catalytic powder is to prepare a deposition solution comprising at least a palladium promoter and an organic or inorganic acid.

It is known from U.S. Patent. No. 5,066,380 that the presence of palladium metal ions in the deposition solution, in addition to the metal ions of the electrocatalytic metal precursor compound, promotes deposition of the electrocatalytic metal onto the metal particles.

Example of suitable palladium metal compounds are palladium halides and palladium nitrate. The concentration of the palladium metal ions in the porous coating solution should be sufficient to promote improved electrocatalyst loading on the metal particles. The palladium precursor compounds when present are, generally, included in an amount sufficient to yield a palladium metal ion concentration in the coating solution of at least 0.001 percent by weight based on the weight of the solution. The palladium metal ion concentration suitably can be 0.001 percent to 5 percent; preferably from 0.005 percent to 2 percent and, most preferably, from 0.01 percent to 0.05 percent, by weight of the coating solution. A weight percent of less than 0.001 percent is generally insufficient to promote deposition of the electrocatalytic metal. A weight percentage greater than percent 5 results in the deposition of an excessive amount of electrocatalytic metal primary phase of the coating on the substrate.

The pH of the deposition solution may be adjusted by inclusion of organic acids or inorganic acids therein. Examples of suitable inorganic acids are hydrobromic acid, hydrochloric acid, sulfuric acid, perchloric acid, and phosphoric acid. Examples of organic acids are acetic acid, oxalic acid, and formic acid. Hydrobromic acid and hydrochloric acid are preferred. The pH range for the deposition solution is, generally, 0 pH to 2.8 pH. Precipitation of hydrous platinum group metal oxide results at higher pHs. A low pH can encourage competing side reactions such as the dissolution of the substrate.

At least one electrocatalytic metal compound soluble in water or an aqueous acid is added to the deposition solution. A suitable electrocatalytic metal is, generally, one that is more noble than the metal employed for the metal particles, that is, the electrocatalytic metal precursor compound has a Gibbs free energy greater than the Gibbs free energy of the metal compound from dissolution of the metal particles, such that non-electrolytic reductive deposition occurs on the metal particles. Preferably, such electrocatalytic metal is a platinum group metal. More details non-electrolytic reductive deposition can be found in U.S. Patent

5,645,930.

The electrocatalytic metal precursor compound can be present in the deposition solution in amounts sufficient to deposit an effective amount of the metal on the metal particles. The concentration of electrocatalytic metal ions in the deposition solution, in terms of weight percent, is, generally, from 0.01 percent to 5 percent, preferably, from 0.1 percent to 3 percent and, most preferably, from 0.2 percent to 1 percent by weight of solution. An electrocatalytic metal ion concentration of greater than 5 percent is not desired, because an unnecessarily large amount of platinum group metal is used to prepare the coating solution. An electrocatalytic metal ion concentration of less than 0.01 percent is not desired, because undesirably long contact times are required.

The optional particulate material is suspended in the deposition solution at a concentration of from 0.002 to 2 percent, preferably, 0.005 to 0.5 percent, and most preferably, 0.01 to 0.2 percent.

After the deposition solution comprising the palladium promoter, the acid, and the optional particulate material is prepared, it is held at an elevated temperature and stirred at a high speed, while a powder comprising support metal particles is added thereto. After a period of time, the electrocatalytic metal precursor compound is added, and the electrocatalytic metal is formed and deposited on the support metal particles with simultaneous partial dissolution of the support metal particles.

The rate at which the electrocatalytic metal deposits to form the porous coating on the metal particles is a function of the solution temperature. The temperature, generally, ranges from 25°C to 90°C. Low temperatures are not practical, since uneconomically long times are required to deposit an effective amount of electrocatalytic metal on the metal particles. Temperatures higher than 90°C are operable, but generally result in an excessive amount of metal deposition and side reactions. A temperature ranging from between 40°C to 80°C is preferred, with 45°C to 65°C being most preferred.

Generally the time allowed for contact between the deposition solution and the metal particles can vary from one minute to 60 minutes. However, it should be understood that the contact time required will vary with deposition solution temperature, electrocatalytic metal concentrations, and palladium ion concentration. Contact times of from 5 minutes to 60

minutes are preferred, with from 10 minutes to 40 minutes being most preferred. Generally, if shorter contact times are desired, the method described herein may be repeated a plurality of times until an effective amount of the platinum group electrocatalytic metals deposit on the surface of the metal particles.

5 The catalytic powder 10 is advantageously used to form electrodes for electrolysis cells. Figure 2 illustrates a magnified view of a portion of an electrode 20 of the present invention. The electrode 20 comprises a conductive metal substrate 21 and a first layer, the first layer comprising a matrix 22 with the above described catalytic powder 10 dispersed therethrough. The porous dendritic nature of the catalytic powder creates a porous surface on
10 the electrode, which in turn reduces the overpotential required for efficient operation of the electrode and electrolytic cells.

Preferably, the conductive metal substrate 21 is nickel, iron, steel, stainless steel, cobalt, copper or silver. The shape of the substrate is not critical and can be, for example, a flat sheet, a curved surface, a punched plate, a woven wire screen, or a mesh sheet.

15 The matrix 22 of the first layer comprises either a platinum group metal oxide or a mixture of a platinum group metal oxide and a valve metal oxide. Platinum group metal oxides include oxides of ruthenium, iridium, rhodium, osmium, platinum, palladium or a mixture of any one or more of these. Valve metal oxides include oxides of titanium, zirconium, tantalum, tungsten, niobium, bismuth, or a mixture of any one or more of these.

20 To make an electrode of the present invention, the above described catalytic powder is mixed with a dispensing medium to form a mixture which is applied to the conductive metal substrate to form a covered substrate. The covered substrate is then baked in the presence of oxygen.

The dispensing medium forms the matrix of the electrode and comprises either a
25 platinum group metal oxide precursor or a mixture of a platinum group metal oxide precursor and a valve metal oxide precursor. Platinum group metal oxide precursors are those materials that form platinum group metal oxides upon baking in the presence of oxygen. Preferred platinum group metal oxide precursors include platinum group metal halides, sulfates, nitrates, nitrites, and phosphates. More preferred are platinum group metal halides, nitrates
30 and phosphates, with platinum group metal chlorides being the most preferred. Valve metal

oxide precursors are those materials that form valve metal oxides upon baking in the presence of oxygen. Preferably, the valve metal oxide precursor is titanium alkoxide, tantalum alkoxide, zirconium acetylacetonate, or niobium alkoxide.

Preferably, the dispensing medium further comprises a solvent. Suitable solvents include methanol, ethanol, 1-propanol, 2-propanol, butanol, or a mixture of any of these.

Preferably, the dispensing medium further includes a compound soluble in alkaline solutions. Examples of such soluble compounds include aluminum chloride and zinc chloride. Such alkaline soluble compounds are useful in generating pores in the coating after they are dissolved in an alkaline solution.

Any appropriate method may be used for dispersing the catalytic powder in the dispensing medium. Examples include mechanical stirring, sonicating, or combinations thereof.

The application of the catalytic powder/dispensing medium mixture can be accomplished using any suitable method. An example is spraying through a nozzle. The spraying forms a platinum group metal loading in the resulting electrode of, generally, 50 $\mu\text{g}/\text{cm}^2$ to 2000 $\mu\text{g}/\text{cm}^2$ calculated as the metal in the "atomic" form. The amount of metal in the electrode is measured by x-ray fluorescence. A preferred loading for both the elemental metal and combined oxide is from 400 $\mu\text{g}/\text{cm}^2$ to 1500 $\mu\text{g}/\text{cm}^2$ with a most preferred loading of from 500 $\mu\text{g}/\text{cm}^2$ to 1000 $\mu\text{g}/\text{cm}^2$. Loadings less than 50 $\mu\text{g}/\text{cm}^2$ are generally insufficient to provide a satisfactory reduction of cell overvoltage. Loadings greater than 2000 $\mu\text{g}/\text{cm}^2$ do not significantly reduce the applied overvoltage when compared to lesser loadings within the preferred range. It should be understood that the effective amount of deposition specified above refers only to loading of the platinum group electrocatalytic metal and metal oxides in the electrode and does not include the amount of the palladium metal promoter which can be used to provide increased loading or any optional secondary electrocatalytic metal or the metal particles.

In a preferred embodiment, the substrate is protected before the mixture is applied thereto, by, for example, electroless nickel plating. Such a process is described in U.S. Patent No. 4,061,802.

A baking step is used to convert the platinum group metal oxide precursor and valve metal oxide precursor to an oxide form. The coated substrate is baked in the presence of oxygen at a temperature of preferably at least 350°C more preferably at least 420°C and even more preferably at least 450°C. Preferably, the coated substrate is baked at a temperature of not more than 550°C more preferably not more than 500°C even more preferably not more than 480°C. Preferably the baking step occurs for anywhere from 30 to 90 minutes. It is important that the coated substrate be baked in the presence of oxygen, be it air or some other oxygen-containing substance, so that the platinum group metal oxide precursor and the valve metal oxide precursor convert to platinum group metal oxide and valve metal oxide. The result is a two-phase first layer of the electrode, one phase being the matrix, and the second phase being the catalytic powder particles dispersed through the matrix.

In a preferred embodiment, the electrode of the present invention further comprises a reinforcement layer 23. Such a reinforcement layer 23 preferably comprises a transition metal or alloy thereof. More preferably, the reinforcement layer is nickel, cobalt, copper, or alloys thereof with boron, phosphorous or sulfur.

To make the optional reinforcement layer, a second electroless plating step, which consists of plating the coated substrate with a transition metal or a transition metal alloy. Such a reinforcement layer helps hold the catalyst powder and matrix together and also helps ensure that the first layer adheres to the substrate. More details forming the reinforcement layer can be found in U.S. Patent No. 5,645,930.

Unless otherwise specified, all parts and percentages are by weight. The following examples are not meant to be limiting.

Examples 1-3: Preparation of Catalytic Powder With Metal Particulate Material

5 A porous coating solution was prepared, with PdCl_2 as palladium promoter and 0.5 N HCl as acid. The solution was heated to a reaction temperature and continuously stirred. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was added as the electrocatalytic platinum group metal compound. The resulting solution was held at the reaction temperature and stirred using a COWLES high-speed disperser, while 3-micron nickel powder (Aldrich) was added. After stirring the mixture at
10 the elevated temperature for a desired contact time, the resulting Ru-coated nickel powder was collected on a filter paper, dried for several hours at 90 °C and weighed. The amount of Ru in the powder was determined using X-ray fluorescence. Table I lists the variables and the results.

Table I

Example	1	2	3
0.5N HCl solution (grams)	500	1420	1577
PdCl_2 (milligrams)	20.9	59.3	6.32
Reaction temp. (°C)	64	61	61.7
RuCl_3 added (grams)	2.095	5.95	2.681
Nickel powder (grams)	35.2	100	100.4
Reaction time (minutes)	15	5	5
Total weight after drying (grams)	28.13	83.7	85.22
Percent Ru in powder	3.1	3.0	3.14

Examples 4-6: Preparation of Catalytic Powder With Metal/Metal Oxide Agglomerates As Particulate Material

A porous coating solution was prepared, with PdCl_2 as palladium promoter and 0.5 N HCl as acid. The solution was heated to a reaction temperature and continuously stirred. RuO_2 was added as the platinum group metal oxide. The resulting solution was held at the reaction temperature and stirred using a COWLES high-speed disperser operated at 3000 rpm, while 3-micron nickel powder (Aldrich) was added. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was then added as the electrocatalytic platinum group metal compound. After stirring the mixture at the elevated temperature for a desired contact time, the resulting Ru-coated nickel powder was dried and weighed. The amount of Ru in the powder was determined using X-ray fluorescence. Table II lists the variables and the results.

Table II

Example	4	5	6
0.5N HCl solution (grams)	1405	1402	1413
PdCl_2 (milligrams)	60	60	60
Reaction temp. ($^{\circ}\text{C}$)	51	52.8	50.6
RuO_2 (grams)	0.714	0.720	0.714
Nickel powder (grams)	38.84	38.63	38.14
RuCl_3 (grams)	8.74	8.75	8.57
Reaction time (minutes)	50	50	110
Total weight after drying (grams)	16.57	16.70	15.98
Percent Ru in powder	26.0	25.86	26.5

Examples 7-9 - Preparation of Cathode With a metal Particulate Material

A 5 inch by 6 inch plate was electroless nickel-plated according to procedures described in U.S. Patent No. 4,061,802. The plate was then sprayed with a mixture of a dispensing medium and a Ru-coated nickel powder (Ru=3.1 percent) dispersed therethrough. The powder weight percent in the spraying mixture was around 10 percent. The platinum group metal oxide precursor in the dispensing medium was RuCl_3 , the valve metal oxide precursor compound in the dispensing medium was titanium isopropoxide. The solvent in the dispensing medium was a combination of methanol and 2-propanol, the compound soluble in alkaline solutions was aluminum chloride or zinc chloride, and the acid used to adjust pH, when used, was HCl gas.

The sprayed sample was allowed to dry at 90°C for 20 minutes and baked at 490°C for 60 min. X-ray fluorescence of the sample was used to determine loading of the metal on the substrate. Table III lists the parameters and results.

Table III

Example	7	8	9
$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (wt. percent)	2.37	2.37	2.37
Ti(isopropoxide) (wt. percent)	6.69	6.69	6.69
Methanol (wt. percent)	76.5	76.5	5.00
2-propanol (wt. percent)	9.73	9.73	81.07
Compound soluble in alkaline solution (wt. percent)	3.43 ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)	3.43 ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)	3.62 ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
HCl gas (wt. percent)	1.28	1.28	1.25
Metal loading ($\mu\text{g}/\text{cm}^2$)	151	133	169

Examples 10-13 - Preparation of Cathode with a Metal/Metal Oxide Agglomerate Particulate Material

A 5 inch by 6 inch plate was electroless nickel-plated according to procedures described in U.S. Patent 4,061,802. The plate was then sprayed with a mixture of a dispensing medium and a Ru/RuO₂-coated nickel powder (Ru=25.86 percent) dispersed therethrough. The powder weight percent in the spraying mixture is around 10 percent. The dispensing medium comprises 2.37 weight percent RuCl₃·xH₂O as the platinum group metal oxide precursor, 2.87 weight percent titanium isopropoxide as the valve metal oxide precursor, 8.86 weight percent methanol and 83.80 weight percent 2-propanol as the solvent, and 2.10 weight percent AlCl₃·6H₂O as the compound soluble in an alkaline solution.

The sprayed sample was allowed to dry at 90°C for 20 minutes and baked at 490°C for 60 min. X-ray fluorescence of the sample was used to determine loading of the metal on the substrate. Table IV lists the parameters and results.

Table IV

Example	10	11	12	13
Percent Ru in catalytic powder	25.86	25.86	25.86	26.0
Metal loading (µg/cm ²)	521	555	766	428

Examples 14-16 - Preparation of Electrodes having a second reinforcement layer

The samples from Examples 7-9 above are coated with the second reinforcement layer of Ni-P by the following steps:

The plates were dipped in the following mixture of solutions for a period of five minutes at ambient temperature: 25cc 0.01 M (NH₄)₂PdCl₄ in methanol, 50cc 0.1 M poly(4-vinylpyridine) in methanol, and 425cc methanol. The coated plates were then dried in a horizontal position at 90°C. The dipping and drying steps were repeated.

Thereafter, the coated plates were placed in a plastic horizontal container with the thread of the plate fitted in a fitting in the bottom of the container. The container was first filled with an aqueous solution containing 36g/l of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ at pH=2.95 for 5-10 minutes to reduce Pd(II) to Pd^0 . The solution was then poured out and 500ml of an electroless nickel-plating solution was then added to the container and electroless plating was conducted for 20 min. The composition of the electroless plating solution is:

NiCl ₂ · 6H ₂ O	17.4g/l
Sodium Citrate	30.24g/l
NaH ₂ PO ₂ · H ₂ O	25.2g/l
NH ₄ Cl	21.26g/l
NH ₄ OH	add to get pH = 8.8

Weight gains for Example 4 (Example 7), Example 5 (Example 8) and Example 6 (Example 9) were 2.63 mg/cm², 3.26 mg/cm², and 2.69 mg/cm², respectively.

To measure the hydrogen potential, the plates were connected to a nickel rod and placed in a caustic bath at an elevated temperature. A platinum plate welded to a nickel rod was used as the anode. Current densities of 0.46 amps per square inch (ASI), 1.0 ASI, and/or 1.09 ASI were applied to the cathode sample and the anode from a rectifier. The potential of the cathode was measured with the aid of a LUGGIN probe with a Hg/HgO reference electrode. The parameters and results were listed in Table V.

Table V

Example	14	15	16
Percent caustic in bath	11.75	11.75	32
Temperature of caustic bath (°C)	70	70	90
Voltage at 0.46 ASI	-0.960	-0.962	-1.007
Voltage at 1.0 ASI	--	-0.979	--
Voltage at 1.09 ASI	--	--	-1.025

Examples 17-20 - Preparation of Electrodes having a Second Reinforcement Layer

The samples from Examples 10-13 above were coated with the second reinforcement layer of Ni-P by the following steps:

Initiation was conducted at 0.8-0.9 amperes at ambient temperature for 2-3 minutes. The plate was then placed in an electroless plating solution for 20-30 minutes. The composition of the electroless plating solution is:

NiCl ₂ x6H ₂ O	17.4 g/l
Sodium Citrate	30.24g/l
NaH ₂ PO ₂ xH ₂ O	25.2g/l
NH ₄ Cl	21.26g/l
NH ₄ OH	add to get pH = 8.8

Weight gains for Example 10 (Example 17), Example 11 (Example 18), Example 12 (Example 19) and Example 13 (Example 20) are 0.550g, 0.578g., 0.683g, and 0.489g, respectively.

Examples 20-23 - Hydrogen Potential Measurements

To measure the hydrogen potential for the plates prepared in Examples 17-20, the plates were connected to a nickel rod and placed in an 11.75 percent caustic bath at 70°C. A

platinum plate welded to a nickel rod was used as the anode. A current density of 0.46 ASI was applied to the cathode plate and the anode from a rectifier. The potential of the cathode was measured with the aid of a LUGGIN probe versus a Hg/HgO reference electrode. The hydrogen potential measurements for Example 17 (Example 20), Example 18 (Example 21), Example 19 (Example 22), and Example 20 (Example 23) are -0.956 volts, -0.960 volts, -0.949 volts and -0.956 volts, respectively.

WHAT IS CLAIMED IS:

1. A catalytic powder comprising:

a plurality of support metal particles comprising a transition metal or an alloy thereof;
and

5 a porous coating surrounding the metal particles, the porous coating comprising an electrocatalytic metal continuous phase.

2. The catalytic powder of Claim 1 wherein the porous coating further comprises a particulate material in admixture with the electrocatalytic metal continuous phase.

3. The powder of Claim 1 wherein the electrocatalytic metal in the porous
10 coating is ruthenium, iridium, osmium, platinum, palladium, rhodium, rhenium, or an alloy thereof.

4. The powder of Claim 2 wherein the particulate material in the porous coating is rhenium oxide, technetium oxide, molybdenum oxide, chromium oxide, niobium oxide, tungsten oxide, tantalum oxide, manganese oxide, lead oxide.

15 5. The powder of Claim 1 wherein the support metal particles are nickel, cobalt, iron, steel, stainless steel, or copper.

6. The powder of Claim 5 wherein the support metal particles have an average diameter of from 0.2 to 20.0 microns.

7. An electrode comprising:

20 a conductive metal substrate; and

a first layer comprising a matrix with a catalytic powder dispersed therethrough, the matrix comprising a platinum group metal oxide or a mixture of a platinum group metal oxide and a valve metal oxide, the catalytic powder comprising support metal particles covered with a porous coating, the porous coating comprising an electrocatalytic metal.

25 8. The electrode of Claim 7 wherein the porous coating further comprises a particulate material in admixture with the electrocatalytic metal.

9. The electrode of Claim 7 wherein the conductive metal substrate is nickel, iron, steel, stainless steel, cobalt, copper, or silver.

10. The electrode of Claim 7 wherein the support metal particles in the catalytic powder are nickel, cobalt, iron, steel, stainless steel, or copper.

5 11. The electrode of Claim 7 wherein the electrocatalytic metal in the porous coating of the first layer is ruthenium, iridium, rhodium, osmium, platinum, palladium, rhenium, or a mixture thereof.

10 12. The electrode of Claim 8 wherein the particulate material in the porous coating of the first layer is a metal oxide particulate material selected from the group consisting of a platinum group metal oxide, rhenium oxide, technetium oxide, molybdenum oxide, chromium oxide, niobium oxide, tungsten oxide, tantalum oxide, manganese oxide and lead oxide.

15 13. The electrode of Claim 7 wherein the platinum group metal oxide in the matrix is ruthenium oxide, iridium oxide, osmium oxide, platinum oxide, palladium oxide or a mixture thereof; and the valve metal oxide in the matrix is titanium oxide, zirconium oxide, tantalum oxide, tungsten oxide, niobium oxide, bismuth oxide, or a mixture thereof.

14. The electrode of Claim 7 further comprising a second reinforcement layer consisting essentially of a transition metal or alloy thereof.

15. The electrode of Claim 14 wherein the transition metal or alloy thereof is nickel, cobalt, copper, or alloys thereof with phosphorous, boron or sulfur.

20 16. A process for making an electrode comprising the steps of:

forming a catalytic powder;

mixing the catalytic powder with a dispensing medium to form a mixture;

applying the mixture to a conductive metal substrate to form a covered substrate; and

baking the covered substrate in the presence of oxygen.

25 17. The process of Claim 16 wherein the catalytic powder is formed by covering a plurality of support metal particles with a porous coating comprising an electrocatalytic metal

in admixture with a particulate material.

18. The process of Claim 17 wherein the porous coating is formed by a nonelectrolytic reductive deposition method, an electrodeposition method or a sintering method.

5 19. The process of Claim 17 wherein the electrocatalytic metal in the porous coating is ruthenium, iridium, rhodium, osmium, platinum, palladium, or a mixture thereof.

20. The process of Claim 17 wherein the particulate material in the porous coating is a metal oxide particulate material selected from the group consisting of a platinum group metal oxide, rhenium oxide, technetium oxide, molybdenum oxide, chromium oxide, niobium
10 oxide, tungsten oxide, tantalum oxide, manganese oxide, lead oxide and a mixture thereof.

21. The process of Claim 16 wherein the applying step is performed using solvent spraying, electrostatic spraying, plasma spraying, or melt spraying.

22. The process of Claim 16 wherein the dispensing medium comprises a mixture of a platinum group metal oxide precursor and a valve metal oxide precursor.

15 23. The process of Claim 22 wherein the platinum group metal oxide precursor is ruthenium chloride; and the valve metal oxide precursor is titanium alkoxide, tantalum alkoxide, zirconium acetylacetonate, or niobium alkoxide.

24. The process of Claim 22 wherein the dispensing medium further comprises aluminum chloride or zinc chloride.

20 25. The process of Claim 24 wherein the dispensing medium further comprises a solvent selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, butanol and a mixture thereof.

26. The process of Claim 16 further comprising the step of plating the coated substrate with a transition metal or a transition metal alloy to form a reinforcement layer.

25 27. The process of Claim 26 wherein the transition metal is nickel, cobalt, copper or an alloy thereof with phosphorous, boron or sulfur.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number
WO 01/28714 A1

(51) International Patent Classification²: **B22F 1/02**,
3/11, C25B 11/03, 11/04

(21) International Application Number: PCT/US00/28563

(22) International Filing Date: 13 October 2000 (13.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/160,545 20 October 1999 (20.10.1999) US

(71) Applicant (for all designated States except US): **THE DOW CHEMICAL COMPANY** [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **TSOU, Yu-Min** [—/US]; 107 Fir Street, Lake Jackson, TX 77566 (US). **MANOR, Edmond, L.** [—/US]; Rt 2 Box 2345, Brazoria, TX 77422 (US).

(74) Agent: **JOZWIAK, Elisabeth, T.**; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.

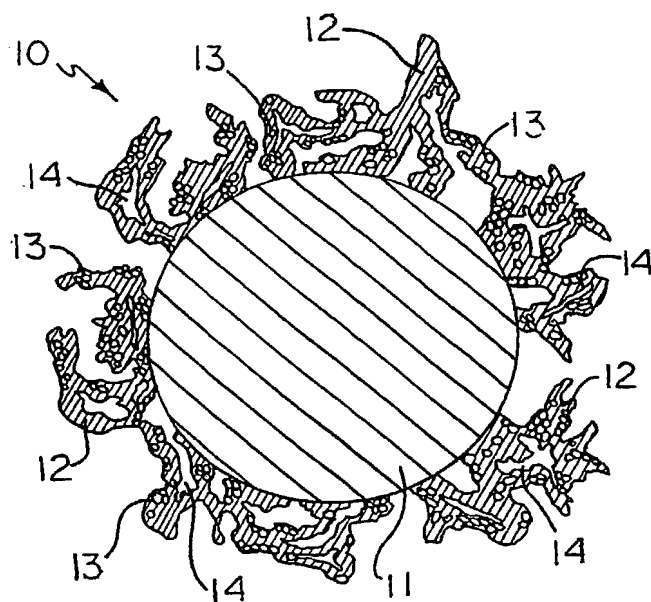
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYTIC POWDER AND ELECTRODE MADE THEREWITH



(57) Abstract: A catalytic powder comprising a plurality of support metal particles with a porous coating (12) surrounding the metal particles (11), the porous coating comprising either an electrocatalytic metal or an electrocatalytic metal continuous phase in admixture with a particulate material (14). An electrode made with the catalytic powder and a method to make the electrode is also disclosed. The present invention is advantageous because the porous coating mixture is first applied to a powder rather than being applied directly to a metal substrate, thereby creating a large internal surface area on the electrode and accordingly, lower overpotential requirements.

WO 01/28714 A1

1 / 2

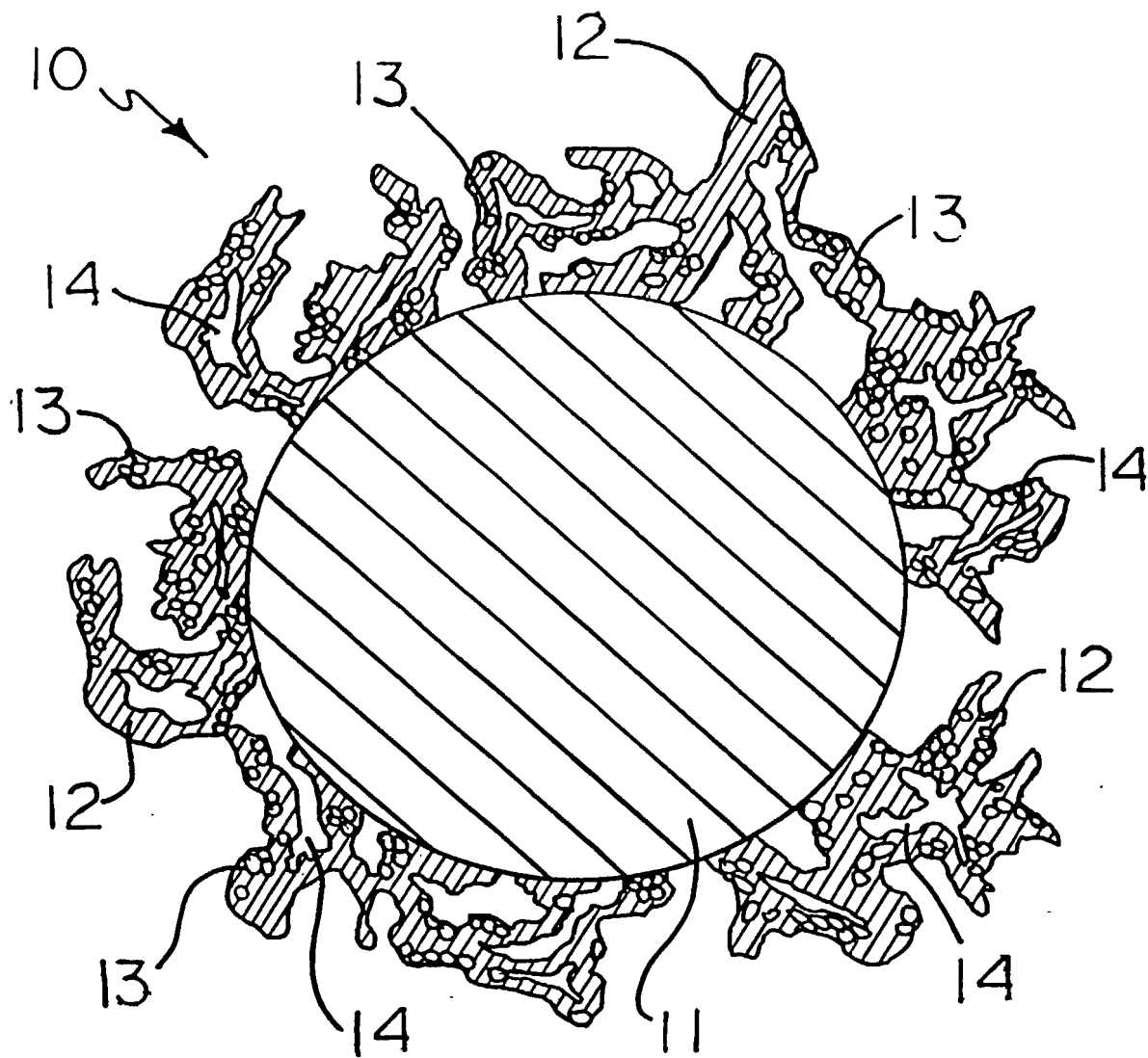


Fig. 1

2 / 2

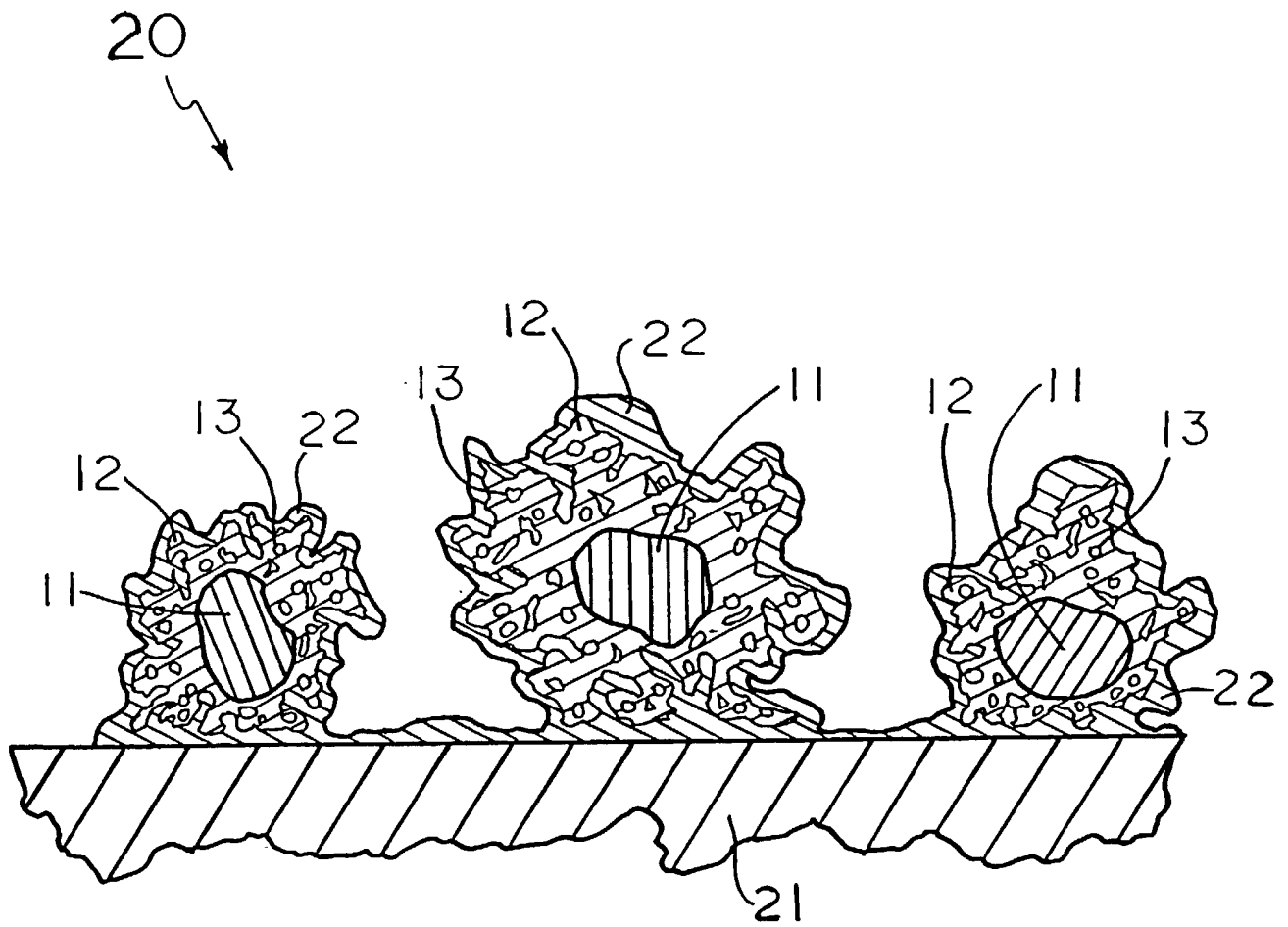


Fig. 2

This Assignment 1000 is in the ENGLISH language and has the same meaning in other languages, with the same 1000 number and R/Date

This Assignment 1000 is in the ENGLISH language and has the same meaning in other languages, with the same 1000 number and R/Date

JUL 22 2002

DECLARATION AND POWER OF ATTORNEY

USA/PCT

As a below named inventor, I hereby declare that:

My residence and Citizenship are as stated below my name. My P.O. (mailing) address is the same as my residence unless otherwise stated.

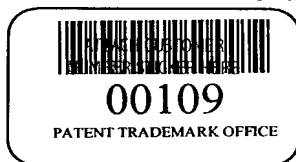
(b) I verily believe I am/we are the original, first and sole/joint inventor(s) of the subject matter that is embraced by and for which a patent is sought on the invention entitled: **CATALYTIC POWDER AND ELECTRODE MADE THEREWITH**

and the specification of which: ☐ is attached hereto ()
(check one)

☒ was filed on **October 13, 2000** as (43040).
Application No. **PCT/US00/28563**
and was amended on

- (c) I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.
- (d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.
- (e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate listed below or §365(a) of any PCT international application that designated at least one country other than the United States of America listed below, and also identify below any other foreign equivalent application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed:
Additional claims for benefit are attached.
- (f) I hereby Claim the benefit under 35 U.S.C. §119 of any United States provisional application(s) or §120 of any United States application(s) listed below:
Additional claims for benefit are attached.

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Address all correspondence to The Dow Chemical Company's appointed counsel at:



This appointment, including the right to delegate this appointment, shall also apply to the same extent it is applicable under the laws of the United States of America to any proceedings established by the Patent Cooperation Treaty.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Inventor(s):

At: 533 Mercer Road
this 22 day of May 2002

Signature: Yu-Min Tsou
Full Name: Yu-Min Tsou
Residence: 533 Mercer Road
Princeton, New Jersey 08540
Country: United States of America NJ
Citizenship: Taiwan USA (mt)
P. O. Address: Same as Residence

At: _____
this _____ day of _____ 20____

Signature: _____
Full Name: _____
Residence: _____

Country: _____
Citizenship: _____
P. O. Address: _____

(☐) Additional names and signatures are attached.

At: Freeport, Texas 77541, USA
this 1 day of May 2002

Signature: Edmond L. Manor
Full Name: Edmond L. Manor
Residence: 2254 FM522
Brazoria, Texas 77422 TX
Country: United States of America
Citizenship: United States of America
P. O. Address: Same as Residence

At: _____
this _____ day of _____ 20____

Signature: _____
Full Name: _____
Residence: _____

Country: _____
Citizenship: _____
P. O. Address: _____